ARTIFICIAL SUPERHYDROPHOBIC SURFACES WITH HIGH AND LOW ADHESION

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1 Introduction

Biomimetics means mimicking biologically inspired design or adaptation or derivation from nature [1]. It involves the understanding of biological functions, structures, principles of various objects found in nature, and the design of various materials and devices of commercial interest. Nature's objects provide an inspiration to humans and important ideas for many revolutionary developments. As an example, superhydrophobic and self-cleaning surfaces which have a high static contact angle (CA) (above 150°) and low contact angle hysteresis (CAH) of less than 10°, such as *Nelumbo nucifera* (lotus) and *Colocosia escuenta*, are found in nature [2]. These surfaces are of commercial interest in various applications such as self-cleaning windows, paints, and textiles to low-friction surfaces for fluid flow and energy conservation [3]. Recent reports have characterized the leaf surfaces at the micro- and nanoscale while separating out the effects of the micro- and nanostructure and wax of hydrophobic leaves on their hydrophobicity [4,5].

Unlike Lotus leaf, certain rose petals are known to be superhydrophobic with high adhesion [6,7]. There also exist rose petals which are superhydrophobic with low adhesion similar to Lotus leaf. The purpose of this study is to fabricate artificial superhydrophobic surfaces with high and low adhesion using a two step molding process and wax evaporation method. It is shown that the pitch values of microstructures and density of nanostructures play an important role in real rose petals and artificial surfaces to control their adhesion properties.

2 Experimental methods

3 Result and Discussion

Figure 1 shows optical micrographs and scanning electron microscopy (SEM) images of two rose petals. In our study, to get stable samples, we dried the petals for SEM measurement. It is reported that during the measurement of real petals using SEM loss of water from the cell occurred, leading to shrinkage on the hierarchical micro- and nanostructures on petals in a high-vacuum chamber [8].

Figure 1 (c) shows optical micrographs of water droplets on the Rosa, *cv*. Bairage petal in the fresh state. As water droplet is deposited on its surface, a high static contact angle (152°) is observed on the petal.When the petal is turned upside down, the water droplet does not drop down, which suggests high adhesion. In the case of droplet on the Rosa, *cv*. Showtime, it also has high static contact angle (167°), but the droplet easily rolls off the surface with a small tilt angle (6°).

To make an artificial superhydrophobic with high adhesion surface, two step molding process and wax evaporation method are used. Figure 2 shows SEM images of microstructured surfaces with three different pitch values and nanoscale morphologies as a function of mass of *n*-hexatriacontane. The pitch value and mass of wax were used to provide high adhesion and low adhesion surfaces.

Each of three microstructured substrate has 23, 105 and 210 μm pitch value with same diameter (14 μm) and height (30 μm) were prepared. Using evaporation method, *n*-hexatriacontane was coated on microstructure.

When it coated with different masses (0.1 and 0.2 $\mu g/mm^2$) applied, density of nanostructure will be changed as shown in bottom row of Figure 2.

Figure 1b shows the SEM micrographs of the two petals. Both petals have hierarchical structure, which means their surface structure consists of nanostructures on microstructures. The low-magnification micrographs show a convex cell form with irregular cuticular folding in the central fields and parallel folding in the anticlinal field of the cells. It is observed that the two rose petals have different spacing (pitch value, P), P-B height of microstructure, and different density of nanostructure. Pitch value (bump density) and P-B height of microstructures are different in the two petals. On the superhydrophobic surface with low adhesion (Rosa, *cv*. Showtime), its microstructure has a smaller pitch value and a larger P-B height compared to the superhydrophobic surface with high adhesion (Rosa, *cv*. Bairage). A smaller value of the ratio of pitch value (P) and P-B height (H) may lead to the Cassie-Baxter regime. If the value of P/H is decreased, it leads to an increase in the propensity of air pocket formation between microstructures, so the water droplet cannot touch its bottom and minimize the contact area between droplet and surface, resulting in high static contact angle, low contact angle hysteresis, and low adhesion. In the case of the superhydrophobic surface with high adhesion, its large pitch value and small P-B height leads to a decrease in contact area, and water can penetrate to the bottom. This is responsible for a decrease in the static contact angle and an increase in contact angle hysteresis and high adhesion.

From the understanding of real rose petals, artificial superhydrophobic surfaces with high and low adhesion were fabricated. The microstructure had 23, 105, and 210 μm pitch values with the same diameter (14 μm) and height (30 μm). To fabricate the nanostructure, various masses of n-hexatriacontane were coated on a microstructure. The nanostructure is formed by three-dimensional platelets of n-hexatriacontane. Platelets are flat crystals, grown perpendicular to the surface. They are randomly distributed on the surface, and their shapes and sizes show some variation.

Figure 3 displays the static contact angle and contact angle hysteresis change on hierarchical structure as a function of mass of *n*-hexatriacontane with different pitch value. In 23 μm pitch value samples, as the mass of n-hexatriacontane increased, the static contact angle increased and the reverse trend was found for the contact angle hysteresis. In superhydrophobic state, their contact angle hysteresis is less than 10°. In 105 μm pitch value sample, high contact angle hysteresis (87°) with superhydrophobic (static contact angle is 152°) state at 0.1 μg/mm^2 mass of *n*-hexatriacontane is found. The effect of microstructure could be explained from the comparison between regime A and B_1.

When *n*-hexatriacontane (0.1 μg/mm^2) coated on flat epoxy, static contact angle increase to hydrophobic state due to nanostructure and it is coated on micropillars with 105 μm pitch value patterned epoxy substrate, the surface is changed to superhydrophobic state since it has hierarchical structure.

Figure 4 shows shape of droplets on hierarchical structure with 105 μm pitch value. Top row is droplets on horizontal substrate with different mass of *n*-hexatriacontane.

When applied 0.2 μg/mm^2 mass of *n*-hexatriacontane on microstructure, superhydrophobic and low adhesion surface with trapped air pocket is obtained. If using less amount of *n*-hexatriacontane (0.1 μg/mm^2), superhydrophobic and high adhesion surface with no air pocket is fabricated. As shown in bottom row of Fig 10, by applying n-hexatriacontane (0.1 μg/mm^2) on a surface with a 105 μm pitch value (regime A), a superhydrophobic surface with high adhesion but no air pocket between microstructures was fabricated. This surface has high contact angle hysteresis (87°) on vertical substrate and water droplet is not dropped down even if the surface is turned upside down state.

4 Conclusion

In summary, for microstructure with large pitch value and small P-B height and nanostructure with low density, water could impregnate between microstructures, but it is still not completely wetted into nanostructure, resulting in high adhesion while maintaining high static contact angle. However, high density of nanostructure even for a larger pitch value may prevent the transition from Cassie–Baxter to Wenzel regime and may lead to an increased propensity of air pocket formation between micro- and nanostructures with low adhesion.

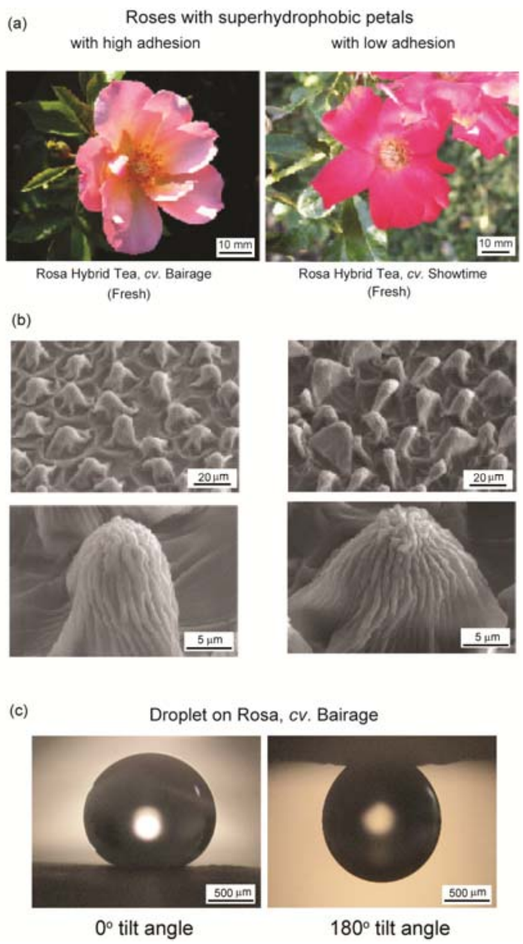

Figure 1. (a) Optical micrographs and (b) SEM micrographs of two roses which have different adhesion properties on its petals: Rosa, *cv*. Bairage and Rosa, *cv*. Showtime. (c) Water droplets on Rosa, cv. Bairage at 0° and 180° tilt angles. Droplet is still suspended when the petal is turned upside down.

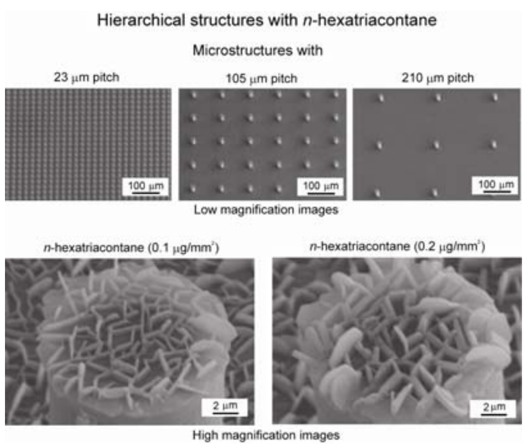

Figure 2. SEM micrographs of the microstructure and nanostructures fabricated with two different masses of *n*-hexatriacontane for hierarchical structure.

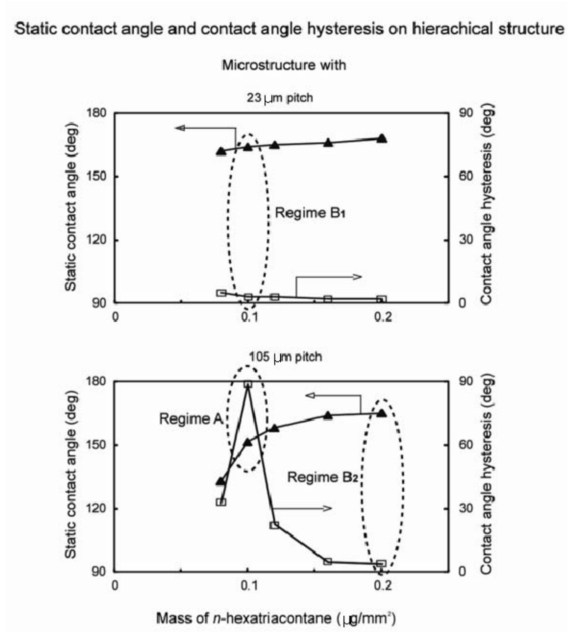

Figure 3. Static contact angle and contact angle hysteresis measured as a function of mass of *n*-hexatriacontane for hierarchical structures with two different pitch values (23 and 105 µm)

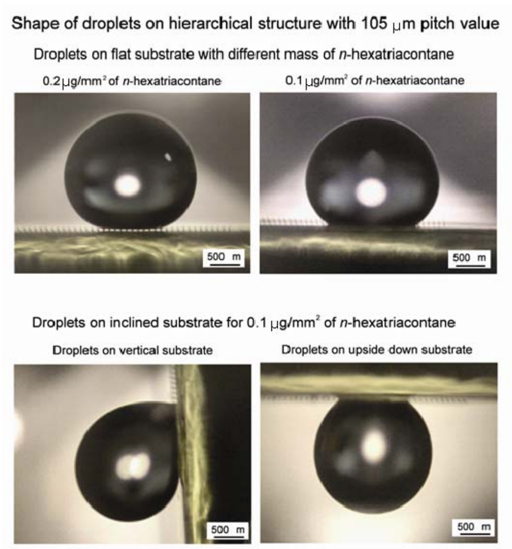

Figure 4. Droplet on horizontal surface of hierarchical structure with 23 μm pitch and *n*-hexatriacontane (0.1 μg/mm2) showing air pocket formation, and Droplet on hierarchical structure with 105 μm pitch and *n*-hexatriacontane (0.1 μg/mm2) and 0.2 μg/mm^2 showing no air pocket and air pocket formation, respectively.

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